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(74) Agent: HARPER, Stephen, D.; Henkel Corporation,
Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA
19406 (US).

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(71) Applicant (*for all designated States except US*): HENKEL
CORPORATION [US/US]; Suite 200, 2500 Renaissance
Boulevard, Gulph Mills, PA 19406 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): SAKO, Ryouzuke
[JP/JP]; 143-3 Idenawa, Hiratsuka-shi, Kanagawa Pref.
254-0915 (JP). UENO, Keiichi [JP/JP]; 2566 Shinomiya,
Hiratsuka-shi, Kanagawa Pref. 254-0014 (JP). HONDA,
Takumi [JP/JP]; 2-18-21 Goten, Hiratsuka-shi, Kanagawa
Pref. 245-0061 (JP). YAMAMOTO, Mayumi [JP/JP];
5-25-27 Seijyo, Setagaya-ku, Tokyo 157-0066 (JP).

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(54) Title: AGENT AND METHOD FOR TREATING METAL SURFACES

(57) Abstract: Metal surfaces may be treated with a chromium-free agent containing one or more polymers of a particular type and one or more V, Zr, Ti, Mo, W, Mn or Ce compounds. The coatings thereby obtained provide excellent corrosion resistance, paint adherence and finger print resistance.

AGENT AND METHOD FOR TREATING METAL SURFACES

Field of the Invention

5 This invention relates to a one-coat-type metal surface treatment agent and method that can be used to form a chromium-free nonchromate coating on — and that impart corrosion resistance, fingerprint resistance, marring resistance, processability, and paint adherence to — sheet coil, castings, and shaped articles (for example, automotive body elements and other automotive parts, construction materials, parts for household electrical appliances) of steel sheet or plated steel sheet such as zinciferous-plated steel
10 sheet. The invention additionally relates to the corresponding surface-treated metals.

Description of the Background Art

Metals such as steel sheet and zinciferous-plated steel sheet are subject to oxidation and corrosion by atmospheric oxygen, moisture, and the ions present in
15 moisture. One technology already known for inhibiting this corrosion comprises forming a chromate coating on the metal surface by bringing the metal into contact with a chromium-containing treatment bath, for example, a chromic acid chromate or phosphoric acid chromate bath. Another known anticorrosion technology comprises the formation of a film or coating by applying a chromium-containing treatment bath to the metal surface
20 followed by drying by heating.

By themselves, the resulting inorganic chromate coatings do provide a short-term antirust activity in relatively mild environments, but their long-term corrosion resistance is unsatisfactory and their corrosion resistance when challenged by harsher environments is also unacceptable. Other problems with these coatings arise in the case
25 of sheet coil on which only a chromate treatment has been executed. Since the resulting coatings are hard and brittle and exhibit a poor lubricity, cutting and/or shaping of such sheet coil is accompanied by the following problems: (i) delamination of the coating, which results in an impaired appearance, and (ii) an inability to carry out shaping or working in a satisfactory manner, which results in the production of cracks in the
30 substrate. Moreover, traces of the fingerprints made by workers during the fabrication process will remain in the subject coatings even after degreasing, leading again to a loss of aesthetics. It is for these reasons that a two-layer treatment is generally carried out in order satisfy the entire spectrum of desired properties, i.e., high corrosion resistance, fingerprint resistance, marring resistance, lubricity, and paint adherence. This two-layer
35 treatment comprises the formation of a chromate coating on the metal surface followed by

the provision of a resin coating on the chromate coating. Finally, aside from the inadequacy of chromate coatings in terms of performance, their treatment baths contain toxic hexavalent chromium, which imposes substantial time, labor, and cost burdens on wastewater treatment. Hexavalent chromium is also present in the coatings produced by these treatments, which has led based on environmental and safety considerations to an ever increasing tendency to avoid the use of these coatings.

So-called resin-chromate — in which chromate and a resin coating are both formed at one time — has been investigated in an attempt to satisfy the entire property spectrum using a one-layer treatment. Japanese Published (Kokoku or Examined) Patent Application Number Hei 4-2672 (2,672/1992) teaches a treatment method comprising the application to the surface of aluminum/zinc-plated steel sheet of a resin composition comprising the blend of a specific water-dispersible or water-soluble resin with a specific amount of hexavalent chromium. Japanese Published (Kokoku or Examined) Patent Application Number Hei 7-6070 (6,070/1995) teaches a metal surface treatment composition containing hexavalent chromium or hexavalent chromium and trivalent chromium (in either case from an inorganic compound) and an acrylic emulsion prepared by polymerization under specific emulsion polymerization conditions. The coatings formed by these treatment methods contain only microamounts of hexavalent chromium, but this hexavalent chromium still gradually elutes from the coating, again raising the environmental and safety problems associated with hexavalent chromium.

Methods that employ non-chromate (chromium-free) treatment baths are known. For example, Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 7-278410 (278,410/1995) teaches a polymer composition and a method for treating metal surfaces wherein the polymer composition contains an acidic compound and a phenolic resin-type polymer with a specific structure. An agent and method for treating metal surfaces are also disclosed in Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 8-73775 (73,775/1996). This agent and method provide an excellent fingerprint resistance. The agent contains at least 2 silane coupling agents having reactive functional groups with specific structures; these reactive functional groups are different from each other but are capable of reacting with one other. Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 9-241576 (241,576/1997) discloses a method and agent for treating metal surfaces wherein the agent contains silane coupling agent with a specific structure and phenolic resin-type polymer with a specific structure. Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 10-1789 (1,789/1998) teaches an agent and method for treating metal surfaces and metals.

thereby treated. This agent contains a specific polyvalent anion and an organic polymer, such as an epoxy resin, acrylic resin, or urethane resin, that contains at least 1 nitrogen atom. Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 10-60233 (60,233/1998) teaches a treatment method that uses two rust preventives (1) and (2) and metals thereby treated. Rust preventive (1) contains a bisphenol A epoxy resin with a specific structure, while rust preventive (2) contains phenolic resin and a specific non-phenolic resin (e.g., polyester).

However, the foregoing chromium-free agents for treating metal surfaces, while offering the advantage of not containing hexavalent chromium, provide an unacceptable corrosion resistance. Even more problematically, they provide a corrosion resistance in marred regions and shaped regions that is much inferior to that provided by chromate coatings. They also provide an unacceptable lubricity, fingerprint resistance, and marring resistance.

In sum, then, no extant nonchromate metal surface treatment agent has the ability to form a coating that can simultaneously provide a metal surface with an excellent corrosion resistance, an excellent paint adherence, and an excellent fingerprint resistance.

Summary of the Invention

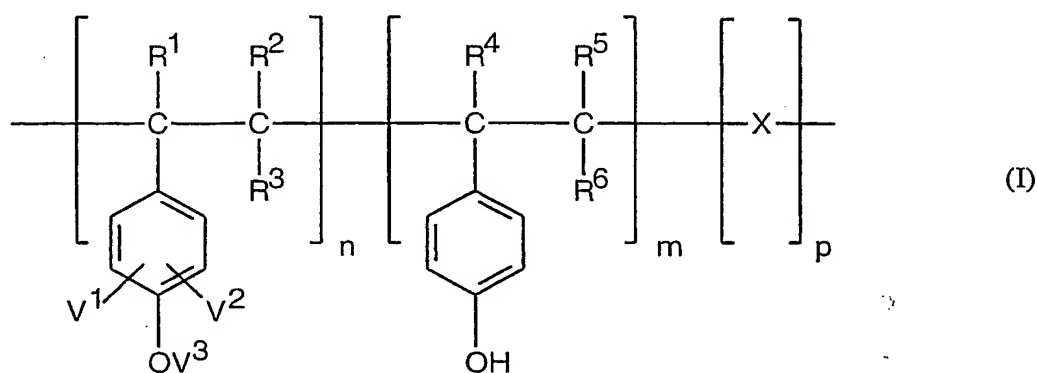
This invention was developed in order to remedy the hereinabove described problems associated with previously known technology. An object of this invention is to provide a metal surface treatment agent that does not contain chromium and that can be used to equip metals with an excellent corrosion resistance, an excellent paint adherence, and an excellent fingerprint resistance. Additional objects of this invention are to provide a metal surface treatment method that uses said agent and metals whose surface has been treated using the inventive agent and method.

As a result of extensive investigations into means for remedying the problems delineated above, the inventors discovered that a highly corrosion-resistant, highly fingerprint-resistant, and strongly paint-adherent coating can be formed by treating metal surfaces with a treatment agent whose essential components are a specific type of metal compound and polymer with a specific structure. This invention was achieved based on this discovery.

Detailed Description of the Invention

In more specific terms, this invention relates to a metal surface treatment agent that comprises

- (a) one or more polymers having general formula (I) or (II) as specified below
and
(b) one or more metal compound or compounds containing at least 1 metal selected from the group consisting of vanadium, zirconium, titanium, molybdenum, tungsten, manganese, and cerium



wherein

R^1 through R^6 are each independently selected from H (hydrogen atom) and C_1 to C_5 alkyl;

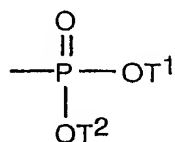
V^1 and V^2 are each independently selected from H (hydrogen atom), $-\text{CH}_2\text{OR}^7$, $-\text{Z}$, $-\text{OZ}$, $-\text{R}^8\text{Z}$, and $-\text{OR}^8\text{Z}$

wherein

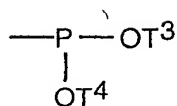
R^7 represents C_1 to C_5 alkyl,

R^8 represents C_1 to C_5 alkylene, and

Z has a general formula as follows



or



wherein T^1 to T^4 are each independently selected from H (hydrogen atom) and C_1 to C_5 alkyl;

5

V^3 is H (hydrogen atom) or $-Z$ wherein this Z is defined as above and wherein, at least one of groups V^1 to V^3 is a Z-containing functional group;

X is a group provided by the opening of an ethylenic double bond of an ethylenic double bond-functional compound that is different from both the compound that provides the structural unit encompassed by the subscript n and the compound that provides the structural unit encompassed by the subscript m ;

10

n is an integer from 2 through 50;

m is 0 or an integer from 1 through 50;

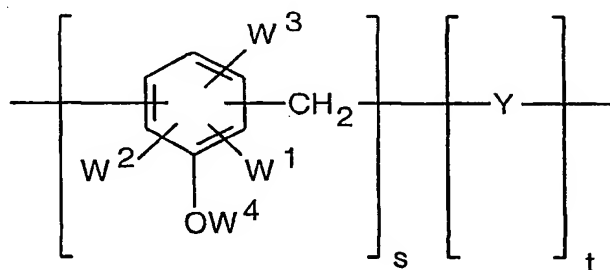
p is 0 or an integer from 1 through 20;

15

$0.1 \leq n/(n + m + p) \leq 1.0$;

$0 \leq m/(n + m + p) \leq 0.9$; and

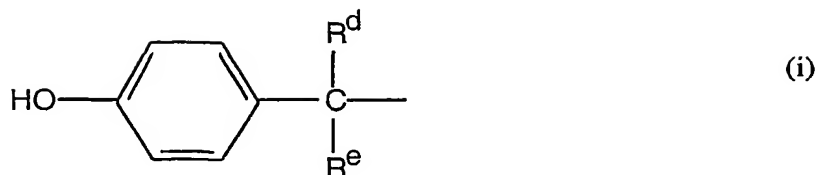
$0 \leq p/(n + m + p) \leq 0.6$;



20

wherein

W^1 through W^3 are each independently selected from H (hydrogen atom), $-CH_2OR^a$, $-Z$, $-OZ$, $-R^bZ$, $-OR^cZ$, and general formula (i)



wherein

R^a , R^d , and R^e are each independently selected from H (hydrogen atom) and C_1 to C_5 alkyl,

5 R^b and R^c are each independently selected from C_1 to C_5 alkylene,

Z is defined as for Z in general formula (I), and

no more than 1 of W^1 through W^3 can be a group with general formula (i);

W^4 represents the hydrogen atom or $-Z$ wherein this Z is defined as above;

at least 1 of groups W^1 through W^4 is a Z -containing functional group;

10 Y is a divalent group as afforded by removal of a hydrogen atom bonded to the aromatic ring carbon of an aromatic compound capable of undergoing addition condensation with formaldehyde, said divalent group being different from the aromatic ring moiety in the structure encompassed by the subscript s , or Y is a divalent group as afforded by the removal of 1 hydrogen atom from each of the

15 2 amino groups in melamine, guanamine, or urea;

s is an integer from 2 through 50; and

t is 0 or an integer from 1 to 20.

20 The inventive metal surface treatment agent preferably also contains (c) an anionic or nonionic organic polymer in order to improve the fingerprint resistance, alkali resistance, and solvent resistance of the coating and obtain additional enhancements in the corrosion resistance of the coating.

This invention additionally relates to a method for treating metal surfaces that is characterized by

25 treating a metal surface with the metal surface treatment agent described above, and drying by heating so the temperature of the metal reaches 50 to 250°C.

This invention further relates to metal that bears a coating formed using said surface treatment method.

30 With regard to the two end groups in general formula (I) for the polymer (a) that is an essential component of the inventive treatment agent, these can be furnished by polymerization initiators such as AIBN (azobisisobutyronitrile), BRO (benzoyl

peroxide), and persulfate salt, and the end structures can vary depending on the polymerization initiator. The two end groups are not critical and can be exemplified by hydrogen atom, phenyl group, $-\text{C}(\text{CH}_3)_2(\text{CN})$, and benzoyloxy.

5 The general formula (I) embodiment of polymer (a) encompasses polymer comprising only the structural unit bounded by the subscript n ; copolymer comprising the structural unit bounded by the subscript n and the structural unit bounded by the subscript m ; copolymer comprising the structural unit bounded by the subscript n and the structural unit bounded by the subscript p ; and copolymer comprising the structural unit bounded by the subscript n , the structural unit bounded by the subscript m , and the structural unit bounded by the subscript p . The structural units bounded by the subscripts n , m , and p may occur in any order relative to one another; for example, their sequence may be $n \rightarrow m \rightarrow p$, $n \rightarrow p \rightarrow m$, $m \rightarrow n \rightarrow p$, $m \rightarrow p \rightarrow n$, $p \rightarrow n \rightarrow m$, $p \rightarrow m \rightarrow n$, $n \rightarrow m$, $n \rightarrow p$, $m \rightarrow n$, and $p \rightarrow n$. Each of these structural units may be bonded in a block configuration, or may be bonded in alternation with another structural unit or units, or may be bonded in a completely random manner. It should be understood that formula (I) encompasses all of these individual embodiments.

 In addition, the structural unit bounded by a particular subscript, for example, the structural unit bounded by the subscript n , may comprise only a single species of said structural unit or may comprise different species of said structural unit.

 The C_1 to C_5 alkyl groups comprising R^1 through R^7 can be exemplified by methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and pentyl.

 The C_1 to C_5 alkylene groups comprising R^8 can be exemplified by methylene, ethylene, propylene, isopropylene, butylene, and pentylene.

25 The C_1 to C_5 alkyl groups comprising T^1 through T^4 can be exemplified by methyl, ethyl, propyl, isopropyl, butyl, and pentyl.

 The definition of X refers to an ethylenic double bond-functional compound that is different from both the compound that provides the structural unit encompassed by the subscript n and the compound that provides the structural unit encompassed by the subscript m . No specific restrictions apply to this ethylenic double bond-functional compound and it can be exemplified by ethylenically unsaturated carboxylic acids such as (meth)acrylic acid, maleic acid, fumaric acid, crotonic acid, and itaconic acid; C_1 to C_8 alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, and 2-ethylhexyl (meth)acrylate;

(meth)acrylamide compounds such as (meth)acrylamide, N-methylol(meth)acrylamide, N-methyl(meth)acrylamide, N-butoxymethyl(meth)acrylamide, and N,N-dimethyl(meth)acrylamide; and other ethylenic double bond-functional compounds such as vinyl acetate, styrene, methylstyrene, acrylonitrile, vinyltoluene, and vinyl chloride.

5 The coating produced from the inventive metal surface treatment agent has a poor durability when the subscript n in general formula (I) is less than 2. A value for n or m in excess of 50 often produces an overly high viscosity and a correspondingly poor stability in water and hence should be avoided. An acceptable corrosion resistance and an acceptable paint adherence are not obtained at values of p in excess of 20.

10 The presence of more than 5 carbons in the alkyl encompassed by R^1 through R^7 causes a strong hydrophobicity to develop with a concomitant decline in the stability in water and hence should be avoided. The presence of more than 5 carbons in the alkylene of R^8 or in the alkyl of T^1 to T^4 causes a similar decline in the stability in water.

15 The two end groups in the general formula (II) embodiment of the polymer (a) that is an essential component of the inventive treatment agent can be methylol, alkoxymethyl (wherein the alkoxy moiety contains from 1 to 5 carbons), W^1 , W^2 , W^3 , or the hydrogen atom.

20 The repeat units bounded by the subscripts s and by t in the polymer with general formula (II) can have, as in the case of general formula (I), a block structure, an alternating-bonded structure, or a random-bonded structure.

 Methyl, ethyl, propyl, isopropyl, butyl, and pentyl are examples of the C_1 to C_5 alkyl represented by R^a , R^d , and R^e in the definition of W^1 to W^3 in general formula (II) for the polymer (a) in the inventive metal surface treatment agent. The C_1 to C_5 alkylene represented by R^b and R^c can be exemplified by methylene, ethylene, propylene, isopropylene, butylene, and pentylene.

25 As stated above, Y in general formula (II) can be a divalent group as afforded by removal of the hydrogen bonded to the aromatic ring carbon of an aromatic compound capable of undergoing addition condensation with formaldehyde, wherein this divalent group is different from the aromatic ring moiety in the structure encompassed by the subscript s . The particular formaldehyde-condensable aromatic compound under consideration is not critical and can be, for example, an aromatic compound such as phenolsulfonic acid, alkylene glycol phenyl ether wherein the alkylene group is C_2 to C_{10} alkylene (e.g., ethylene or propylene), β -naphthol, naphthalenesulfonic acid, toluene, xylene, aniline, acetanilide, thiophenol, thiophene, furfural, or furfuryl alcohol.

A value less than 2 for s in general formula (II) results in a poor corrosion resistance by the coating, while values greater than 50 for s result in an overly high viscosity and a correspondingly poor stability in water and hence should be avoided. An acceptable corrosion resistance and an acceptable paint adherence are usually not obtained when the subscript t has a value above 20. The presence of more than 5 carbons in the alkyl represented by R^a , R^d , R^e , T^1 , T^2 , T^3 , and T^4 results in a strong hydrophobicity with a corresponding decline in the stability in water. The presence of more than 5 carbons in the alkylene represented by R^b and R^c similarly results in a reduced stability in water.

While it should be understood that this invention is not bound to a particular synthesis method, the polymer with general formula (I) can be synthesized, for example, by synthesizing polymer with general formula (I) in which $V^1 = V^2 = V^3 = H$ and then making appropriate modifications to V^1 , V^2 , and V^3 . Polymer (I) in which $V^1 = V^2 = V^3 = H$ can itself be synthesized by the appropriate homopolymerization or copolymerization by the usual methods of monomer that will provide the structural unit bounded by the subscript n in which $V^1 = V^2 = V^3 = H$, monomer that will provide the structural unit bounded by the subscript m when this structural unit is to be present, and monomer that will provide the structural unit bounded by the subscript p when this structural unit is to be present.

The polymer with general formula (II) can generally be synthesized, for example, by appropriate modification of W^1 , W^2 , W^3 , and W^4 after synthesis of the polymer by reacting formaldehyde, monomer that is a source of Y , and phenolic monomer in which $W^1 = W^2 = W^3 = W^4 = H$ or $W^1 = W^2 = W^4 = H$ and W^3 has general formula (i). Again, however, this invention is not bound to a particular method for synthesizing polymer with general formula (II).

The various substituents can be introduced in the case of general formula (I) by the usual methods. As a general matter, the $-CH_2OR^7$ group can be introduced by the reaction of formalin and alcohol with phenolic hydroxyl-functional polymer, e.g., polyhydroxystyrene.

Introduction of the phosphonic acid group $(-P(=O)(OH)_2)$ directly onto the aromatic ring can be carried out, for example, by hydrolysis following a dealkylhalogenation reaction between a trialkyl phosphite $(R-P(=O)(OR)_2)$ and a ring-halogenated phenolic hydroxyl-functional polymer, e.g., ring-halogenated polyhydroxystyrene. Introduction of the phosphonic acid group $(-P(=O)(OH)_2)$ directly onto the aromatic ring can also be effected by hydrolysis following dehydrohalogenation by the action of P^+OCl_2 (produced by the reaction of phosphorus oxychloride $POCl_3$ with

a Lewis acid such as AlCl_3) on a phenolic hydroxyl-functional polymer, e.g., polyhydroxystyrene. Introduction of the phosphinic acid group ($-\text{P}(\text{OH})_2$) directly onto the aromatic ring can be achieved, for example, by hydrolysis following dehydrohalogenation by the action of P^+Cl_2 (produced by the reaction of phosphorus trichloride with a Lewis acid such as AlCl_3) on a phenolic hydroxyl-functional polymer, e.g., polyhydroxystyrene.

Introduction onto the aromatic ring of the phosphonic acid group across an intervening alkyl group can be effected, for example, by hydrolysis following a dealkylhalogenation reaction between trialkyl phosphite and a ring-haloalkylated phenolic hydroxyl-functional polymer, e.g., ring-haloalkylated polyhydroxystyrene. Introduction onto the aromatic ring of the phosphinic group across an intervening alkyl group can be carried out, for example, by (i) synthesis of a ring-chloroalkylated product through the reaction of a chloroalkyl methyl ether (e.g., chloromethyl methyl ether $\text{CH}_3\text{OCH}_2\text{Cl}$) with a phenolic hydroxyl-functional polymer such as polyhydroxystyrene and (ii) running a dehydrochlorination reaction between the ring-chloroalkylated product and phosphonous acid $\text{HP}(\text{OH})_2$.

Introduction onto the aromatic ring of a phosphonic acid group across an intervening oxygen atom can be carried out, for example, by (i) reacting phosphorus pentachloride with a phenolic hydroxyl-functional polymer, e.g., polyhydroxystyrene, in order to convert the phenolic hydroxyl to $-\text{O}-\text{PCl}_4$ and (ii) hydrolyzing the product obtained in (i). Introduction onto the aromatic ring of a phosphinic acid group across an intervening oxygen atom can be accomplished, for example, by hydrolysis following a dehydrochlorination reaction between phosphorus trichloride and a phenolic hydroxyl-functional polymer, e.g., polyhydroxystyrene.

In the case of general formula (II) the various substituents can again be introduced by the usual methods and typically will be introduced by the same methods used for substituent introduction in the case of general formula (I).

Component (b) is another essential component of the inventive treatment agent and comprises a metal compound or compounds containing at least 1 metal selected from the group consisting of vanadium, zirconium, titanium, molybdenum, tungsten, manganese, and cerium. The metal compound (b) can be, for example, the oxide or hydroxide of the foregoing metals, a complex compound thereof, or the salt of an inorganic or organic acid. Component (b) preferably has a good compatibility with polymer (a).

The metal compound (b) can be specifically exemplified by vanadium pentoxide V_2O_5 , vanadium trioxide V_2O_3 , vanadium dioxide VO_2 , metavanadic acid HVO_3 , ammonium metavanadate, sodium metavanadate, vanadium oxysulfate $VOSO_4$, vanadium oxyacetylacetonate $VO(OC(CH_3)=CHCOCH_3)_2$, vanadium acetylacetonate $V(OC(CH_3)=CHCOCH_3)_3$, vanadium oxytrichloride $VOCl_3$, vanadium trichloride VCl_3 , zirconyl nitrate $ZrO(NO_3)_2$, zirconyl sulfate, zirconyl acetate, ammonium zirconyl carbonate $(NH_4)_2(Zr(CO_3)_2(OH)_2)$, fluozirconic acid H_2ZrF_6 , titanyl sulfate $TiOSO_4$, diisopropoxytitanium bisacetylacetonate $(C_5H_7O_2)_2Ti(OCH(CH_3)_2)_2$, the reaction product of lactic acid and titanium alkoxide, fluotitanic acid H_2TiF_6 , titanium lactate $Ti(OH)_2(C_3H_5O_3)_2$, molybdic acid H_2MoO_4 , ammonium molybdate, sodium molybdate, molybdophosphoric acid compounds such as ammonium molybdophosphate $(NH_4)_3(PO_4Mo_{12}O_{36}) \cdot 3H_2O$ and sodium molybdophosphate $Na_3(PO_4 \cdot 12MoO_3) \cdot nH_2O$, metatungstic acid $H_6(H_2W_{12}O_{40})$, ammonium metatungstate $(NH_4)_6(H_2W_{12}O_{40})$, sodium metatungstate, paratungstic acid $H_{10}(W_{12}O_{46}H_{10})$, ammonium paratungstate, sodium paratungstate, permanganic acid $HMnO_4$, potassium permanganate, sodium permanganate, manganese dihydrogen phosphate $Mn(H_2PO_4)_2$, manganese nitrate $Mn(NO_3)_2$, manganese sulfate, manganese fluoride, manganese carbonate, manganese acetate, cerium acetate $Ce(CH_3CO_2)_3$, cerium nitrate, and cerium chloride.

The use of at least two different metal compounds (b) is even more effective for improving such properties as the corrosion resistance and alkali resistance. An even more substantial improvement in these properties can be obtained when at least 1 of the metal compounds (b) is a vanadium compound, and in the most preferred embodiment for improving these properties this vanadium compound contains vanadium in the trivalent or tetravalent oxidation state.

A trivalent or tetravalent vanadium compound can be provided in the inventive treatment agent by simply using a trivalent or tetravalent vanadium compound, e.g., as described above, or by the preliminary reduction of a pentavalent vanadium compound to the trivalent or tetravalent compound through the use of a reducing agent. The reducing agent used for this purpose may be inorganic or organic, but is preferably organic. More preferably the reducing agent is (e) an organic compound containing at least 1 species of functional group selected from the set consisting of the hydroxyl group, carbonyl group, carboxyl group, phosphoric acid group $-OP(=O)(OH)_2$, phosphonic acid group, primary amino group, secondary amino group, tertiary amino group, and amide group. It is particularly preferable for the reducing agent to be a water-soluble organic compound.

The aforementioned reducing agent (e), i.e., an organic compound containing at least 1 species of functional group selected from the set consisting of the hydroxyl group, carbonyl group, carboxyl group, phosphoric acid group ($-\text{OPO}_3\text{H}_2$), phosphonic acid group ($-\text{PO}_3\text{H}_2$), primary amino group, secondary amino group, tertiary amino group, and amide group, can be exemplified by alcohols such as methanol, ethanol, isopropanol, and ethylene glycol; aldehydes such as formaldehyde, acetaldehyde, furfural, and glyoxal; carbonyl compounds such as acetylacetone, ethyl acetoacetate, dipivaloylmethane, and 3-methylpentanedione; organic acids such as formic acid, acetic acid, propionic acid, tartaric acid, ascorbic acid, gluconic acid, citric acid, and malic acid; amines such as triethylamine, triethanolamine, ethylenediamine, pyridine, imidazole, pyrrole, morpholine, and piperazine; acid amides such as formamide, acetamide, propionamide, and N-methylpropionamide; amino acids such as glycine, alanine, proline, and glutamic acid; monosaccharides such as glucose, mannose, and galactose; naturally occurring polysaccharides such as maltose, sucrose, starch, and cellulose; organophosphoric acids such as aminotri(methylenephosphonic acid), 1-hydroxyethylidene-1,1'-diphosphonic acid, ethylenediaminetetra(methylenephosphonic acid), and phytic acid; naturally occurring polymers such as gallic acid, tannic acid, humic acid, ligninsulfonic acid, and polyphenols; synthetic polymers such as polyvinyl alcohol, polyethylene glycol, polyacrylic acid, polyacrylamide, polyethyleneimine, and water-soluble nylons; and aminocarboxylic acids such as EDTA.

Additional enhancements in the corrosion resistance, fingerprint resistance, alkali resistance, and solvent resistance of the coating can be secured by the presence in the inventive treatment agent of (c) an anionic or nonionic organic polymer as an additional component. This organic polymer (c) is preferably compatible with the other components (i.e., the polymer (a) and metal compound (b)) and preferably is soluble in the aqueous medium or capable of forming a uniform and stable dispersion in the aqueous medium, or is capable of forming a uniform and stable dispersion in the aqueous medium in the presence of an emulsifying agent, for example, surfactant.

Since the polymer (a) is anionic in water, the presence of a cationic organic polymer would result in charge attenuation and a lack of stability, and it is for this reason that an anionic or nonionic species is used for the organic polymer (c).

The anionicity of the organic polymer (c) is provided by the presence therein of an anionic functional group, while the nonionicity of (c) is provided by the presence therein of a nonionic functional group. While the type of anionic functional group is not critical, this group can be exemplified by carboxyl group, sulfonic acid group,

phosphoric acid group, phosphonic acid group, thiol group, silanol group, and salts of the foregoing acid groups. The type of nonionic functional group is also not critical; this group can be exemplified by hydroxyl group, amide group, and polyoxyethylene chain. The organic polymer (c) can contain only a single species of the aforementioned functional groups or may contain two or more species of the aforementioned functional groups.

The polymeric structure of the organic polymer (c) is not critical and (c) can be, for example, a urethane resin, epoxy resin, polyester resin, polyamide resin, or resin as afforded by the (co)polymerization of ethylenically double bond-functional monomer (e.g., acrylic resin or vinyl resin).

The organic polymer (c) produced by the (co)polymerization of ethylenic double bond-functional monomer can be, for example, the homopolymer or copolymer of monomer bearing an anionic or nonionic functional group, e.g., (meth)acrylic acid, maleic acid, crotonic acid, itaconic acid, fumaric acid, vinylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid, phosphonyloxymethyl (meth)acrylate, phosphonyloxyethyl (meth)acrylate, vinylphosphonic acid, vinyl mercaptan, 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, (meth)acrylamide, N-methylol(meth)acrylamide, and polyethylene glycol (meth)acrylate. The organic polymer (c) can also be a copolymer of the foregoing monomer with alkyl (for example, C₁ to C₈) acrylate, ethylene, styrene, or acrylonitrile.

Urethane resin-type (c) can be, for example, water-soluble isocyanate prepolymer or the polycondensate of polyisocyanate and a polyol such as a polyester polyol, polyether polyol, or polycarbonate polyol wherein one of the starting components is polyol containing anionic or nonionic functionality.

Epoxy resin-type (c) can be, for example, epoxy resin as afforded by the introduction of anionic or nonionic functionality through the modification of epoxy resin containing residual glycidyl groups.

Polyester resin-type (c) can be, for example, polyester produced from polyol containing anionic or nonionic functionality or dibasic acid containing anionic or nonionic functionality.

Polyamide resin-type (c) can be, for example, polyamide resin produced using polyoxyethylene chain-containing diamine as a starting component or the material produced by the partial or complete methylolation of the H in the NHCO- moiety in a polyamide resin followed by partial oxidation to give the carboxyl group.

Additional enhancements in corrosion resistance and adherence to topcoat can be obtained by the presence in the inventive surface treatment agent of a fluorine compound (d) as an additional component. This is due to etching of the substrate during the application and drying steps with a corresponding acceleration of the coating deposition reactions.

This fluorine compound (d) encompasses hydrofluoric acids, metal fluorides, and complex fluorides and can be specifically exemplified by hydrofluoric acid, fluoboric acid, fluosilicic acid, fluozirconic acid, fluotitanic acid, tin fluoride, ferrous fluoride, and ferric fluoride.

The mass ratio between the constituent components of the inventive surface treatment agent, expressed as metal compound (b) (as metal)/polymer (a), is preferably from 0.005 to 2.0 and more preferably is from 0.01 to 1.0. The corrosion resistance will generally be inadequate when this mass ratio falls below 0.005. When this mass ratio exceeds 2.0, the coating will assume a brittle character that will prevent the desired properties from appearing.

When the organic polymer (c) is used, it should be used at an organic polymer (c)/polymer (a) mass ratio preferably of 0.05 to 20 and more preferably 0.1 to 10. A satisfactory corrosion resistance will generally not be manifested when this mass ratio falls below 0.05 or exceeds 20.

In the case of the fluorine compound (d), this component is used preferably at 0.1 to 100 g/L as the F concentration in 1 liter of treatment bath and more preferably is used at from 0.2 to 50 g/L as the F concentration in 1 liter of treatment bath.

The corrosion resistance, solvent resistance, and chemical resistance of the produced coating can also be improved by the addition to the inventive surface treatment agent of an organic or inorganic crosslinker capable of crosslinking polymer (a) and/or organic polymer (c). Usable as the organic crosslinker are epoxy-type crosslinkers, melamine-type crosslinkers, aldehyde-type crosslinkers, and isocyanate-type crosslinkers. In addition to the metal compounds specified for use in this invention, the inorganic crosslinker can be, for example, a compound of a metal such as iron, cobalt, nickel, niobium, tantalum, or zinc.

The crosslinker is used preferably at from 0.05 to 30 mass parts per 100 mass parts of the total nonvolatile component and more preferably at from 0.1 to 20 mass parts per 100 mass parts of the total nonvolatile component. The desired effects from the crosslinker will typically be inadequate at below 0.05 mass part, while the stability of the treatment agent will ordinarily be diminished at more than 30 mass parts.

For the purposes of this invention, the total nonvolatile component is the component remaining after the surface treatment agent has been dried by heating for 2 hours at 110°C.

5 The corrosion resistance of the coating can be improved still further and its physical properties (for example, the tensile strength) can be adjusted by the addition to the inventive surface treatment agent of a water-dispersible silica sol and/or metal sol, e.g., alumina sol, zirconia sol, etc. When such a component is added, it is preferably added at from 5 to 40 mass% of the total nonvolatile component and more preferably at from 10 to 30 mass% of the total nonvolatile component.

10 Wax can be added to the inventive surface treatment agent in order to improve the lubricity, processability, and mar resistance of the coating, said wax being selected from waterborne waxes such as olefin waxes, e.g., polyethylene wax and polypropylene wax; ester waxes, e.g., carnauba wax, rice wax, candelilla wax, and lanolin; and hydrocarbon waxes, e.g., microcrystalline wax. This component is added
15 preferably at from 0.5 to 30 mass% of the total nonvolatile component and more preferably at from 1 to 20 mass% of the total nonvolatile component.

The inventive surface treatment agent may also contain, within a range that does not impair the objects of the invention, powdered polymer, e.g., polymethyl methacrylate, polystyrene, or melamine, as slip agent or delustrant.

20 The solvent used in the surface treatment agent of this invention will be made up mainly of water, but a water-soluble organic solvent, e.g., an alcohol, ketone, or glycol ether solvent, can be used as necessary or desired in order to improve the dry compatibility of the coating.

25 In addition to the components already considered above, the inventive surface treatment agent may also contain — within a range that does not impair the objects of the invention or the properties of the coating — additives such as surfactant, defoamer, leveling agent, germicide/bactericide, and colorant.

The surface treatment method of this invention will now be considered in detail.

30 The treatment steps preceding the inventive treatment are not particularly restricted, but the inventive treatment will generally be preceded by cleaning with hot water, solvent, or alkaline or acidic degreaser in order to remove oil and contaminants adhering on the substrate. This cleaning can be followed, as necessary or desired, by surface conditioning with acid or base. Cleaning of the substrate surface is preferably

followed by a water rinse in order to the extent possible to avoid leaving residues of the cleaner on the substrate surface.

The essential elements of the treatment method under consideration comprise application of the inventive surface treatment agent on the surface of the metal substrate followed by drying by heating to 50 to 250°C, but the nature of the particular
5 coating technology and drying technology is not critical.

The following application technologies will typically be used: roll coating, in which the treatment agent is applied to the substrate surface by transfer from a roll; broadcasting of the treatment agent over the substrate surface using, for example, a
10 shower ring, followed by roll squeegee; dipping the substrate in a treatment bath; or spraying the treatment agent on the substrate. While the temperature of the treatment bath again is not specifically restricted, the treatment temperature is preferably from 0 to 60°C and is more preferably from 5 to 40°C given that the solvent for the inventive treatment agent is mainly water.

The pH of the treatment bath can be freely adjusted — using inorganic acid, organic acid, ammonia, amine, etc. — into the pH range in which the treatment agent components are stable. However, when one considers the impaired operability that occurs due to overetching of the substrate metal (effect of the substrate metal that becomes dissolved in the treatment bath), the range of 2 to 11 is preferred, the range of 3 to 10 is
20 more preferred, and the range of 4 to 9 is particularly preferred.

When the drying process does not involve curing of the polymer (a) and/or the organic polymer (c) but rather is carried out just in order to remove adhered water, the drying process need not include heating and can be carried out by physical removal by, for example, air-drying or air blowing. Drying by the application of heat,
25 however, will be required when it is desired to accelerate cure of the polymer (a) and/or the organic polymer (c) or enhance the quality of coating by softening. When heating is used, the heating temperature will preferably be from 50 to 250°C and more preferably from 60 to 220°C.

The coating is preferably deposited at from 30 to 5,000 mg/m² as the total mass of the coating and more preferably at from 50 to 3,000 mg/m² as the total mass of the coating. A satisfactory corrosion resistance and adherence to topcoat are ordinarily not obtained at less than 30 mg/m², while values in excess of 5,000 mg/m² often result in the production of cracks in the coating and a reduced adherence by the coating itself.

It is believed (without wishing to be bound by theory) that during
35 application to the substrate metal and drying thereon the inventive treatment agent acts to

provide the substrate with an excellent corrosion resistance and paint adherence (i) by reacting with the surface of the metal substrate, which results in the formation of a highly adherent coating, and (ii) by the formation of a coating by the resin component of the treatment agent.

5 More specifically, the phosphorus-containing acid group in the polymer (a) and the metal ion in the metal compound (b) are thought to react with the surface of the substrate metal, which results in the formation of insoluble salts or insoluble compounds that deposit on and adhere to the surface. In addition, during the drying step polymer (a) is believed to undergo self-crosslinking through intermolecular condensation, 10 or the metal compound (b) acts as a crosslinker for the polymer (a), and as a consequence film formation occurs with the production of a fine, dense three-dimensional structure.

The excellent corrosion resistance of the resulting coating is believed to be due to the excellent adherence to substrate generated by the phosphorus-containing acid group in the polymer (a), the barrier effect produced by the coating for the metal 15 surface, and the following mechanisms. The polymer (a) specified by this invention is a resonance structure-containing compound that is resonance stabilized. It and the specified transition metal compound (b) have the ability, through their π orbitals, to delocalize the electrons produced by corrosion and thereby secure and maintain a uniform surface potential and provide an excellent corrosion resistance not only in flat regions, but also in 20 marred regions and at end surfaces and edges. Moreover, vanadium, tungsten, and molybdenum in particular have an oxidative function like that of chromium and are able to consume, as reducing electrons, the electrons produced by the anode reaction of the corrosion reactions. This provides additional enhancements in the corrosion resistance.

25 The coating formed by the inventive treatment agent also exhibits an excellent processability, shapeability, and slideability due to the fact that its main component is organic resin.

Examples

1. Substrates

- 30 A : electrogalvanized steel sheet (sheet thickness = 0.8 mm)
B : hot-dip galvanized steel sheet (sheet thickness = 0.8 mm)
C : 55% Al/Zn-plated steel sheet (sheet thickness = 0.5 mm)
D : A-3004 Al/Mn alloy (sheet thickness = 0.15 mm)

2. Treatment agents

- 35 (1) Treatment agent components

Polymer (a): a1 through a5, which corresponded to general formula (I), are reported in Table 1, while a6 through a12, which corresponded to general formula (II), are reported in Table 2.

5

Table 1.

	structural formula	
a1	$\left(\text{C}_6\text{H}_4(\text{OPO}_3\text{H}_2) \right)_n \left(\text{C}_6\text{H}_4(\text{OH}) \right)_m$	$n = 20,$ $m = 20$
a2	$\left(\text{C}_6\text{H}_4(\text{OPO}_3\text{H}_2) \right)_{n1} \left(\text{C}_6\text{H}_4(\text{OH})(\text{CH}_2\text{OH}) \right)_{n2}$	$n1 = 5,$ $n2 = 10$
a3	$\left(\text{C}_6\text{H}_4(\text{OH})(\text{PO}_3\text{H}_2) \right)_n$	$n = 40$
a4	$\left(\text{C}_6\text{H}_4(\text{OH})(\text{OPO}_3(\text{CH}_3)_2) \right)_{n1} \left(\text{C}_6\text{H}_4(\text{OH})(\text{CH}_2\text{OC}_4\text{H}_9) \right)_{n2} \left(\text{C}_6\text{H}_4(\text{OH})(\text{SO}_3\text{H}) \right)_p$	$n1 = 30,$ $n2 = 10$ $p = 20$
a5	$\left(\text{C}_6\text{H}_4(\text{OH})(\text{CH}_2\text{PO}_3\text{H}_2) \right)_n \left(\text{C}_6\text{H}_4(\text{OH})(\text{COOH}) \right)_p$	$n = 40,$ $p = 10$

Table 2.

	W ⁴	W ¹	W ²	W ³	s	source of Y
a6	PO ₃ H ₂	H	H	H	12	---
	H	H	H	H	18	
a7	PO ₃ H ₂	CH ₂ OH	H	H	4	---
	H	CH ₂ OC ₃ H ₇	H	H	16	
a8	H	C(CH ₃) ₂ C ₆ H ₅ OH	PO ₃ H ₂	CH ₂ OH	15	---
	H	CH ₂ OH	H	H	5	
a9	H	OPO ₃ H ₂	CH ₂ OH	H	2	sulfonated phenol (sulfonation rate = 40%) t = 10
	H	H	H	H	18	
a10	H	(CH ₂) ₂ PO ₃ H ₂	H	H	3	furfural, t = 2
a11	PO ₃ H ₂	H	H	H	10	toluene, t = 3
a12	PO ₃ H ₂	C(CH ₃) ₂ C ₆ H ₅ OH	CH ₂ OH	H	30	aniline, t = 20

5

The following metal compounds (b) were used in the working and comparative examples.

- b1 : (NH₄)VO₃
- b2 : product of the reduction of V₂O₅ by tartaric acid
- b3 : product of the reduction of (NH₄)VO₃ by glucose
- b4 : VO(C₅H₇O₂)₂
- b5 : (NH₄)₆Mo₇O₂₄·4H₂O
- b6 : 3(NH₄)₂O·12WO₃·nH₂O
- b7 : (NH₄)₂[Zr(CO₃)₂(OH)₂]
- b8 : H₂TiF₆
- b9 : MnCO₃

10

15

Component b2 was synthesized by mixing V₂O₅ and tartaric acid at a 5/1 mass ratio; adding distilled water to adjust to 2 mass% solids; and then heating the mixture for 2 hours at approximately 50°C.

Component b3 was synthesized by mixing $(\text{NH}_4)\text{VO}_3$ with D-glucose in a 1/1 mass ratio; adding distilled water to adjust to 10 mass% solids; and then heating for 2 hours at approximately 70°C.

The following organic polymers (c) were used in the working and comparative examples.

- c1 : acrylic emulsion (POLYZOL AP-6530 from Showa Highpolymer Co., Ltd.)
- c2 : acrylic emulsion (ACRYSET SC-548 from Nippon Shokubai Co., Ltd.)
- c3 : anion-modified epoxy resin (ADEKA Resin EM-0433 from Asahi Denka Kogyo Kabushiki Kaisha)
- c4 : waterborne polyurethane (SUPERFLEX 150 from Dai-ichi Kogyo Seiyaku Co., Ltd.)

The following fluorine compounds (d) were used in the working and comparative examples.

- d1 : HF
- d2 : H_2ZrF_6
- d3 : H_2TiF_6
- d4 : H_2SiF_6

The other components used in the working and comparative examples were as follows.

- e1 : colloidal silica (SNOWTEX N from Nissan Chemical Industries, Ltd.)
- e2 : waterborne wax (CHEMIPPEARL W700 from Mitsui Chemicals, Inc.)

(2) Treatment agent preparation

The polymer (a), metal compound (b), and fluorine compound (d), in each case as the 10 to 20% aqueous solution, were mixed with each other. This was followed by the addition of the organic polymer (c) and other component (e), in each case as the 20 to 40% aqueous solution. This addition was followed by adjustment to the specified concentration with deionized water.

3. Treatment sequence

- (1) Degreasing

(i) The substrate was degreased using PALKLIN 364S, an alkaline degreaser from Nihon Parkerizing Co., Ltd., by spraying the 20 g/L bath at 60°C for 10 seconds using a spray pressure of 50 kPa. Degreasing was followed by rinsing with a 10-second spray of water.

(ii) The substrate was degreased using FINECLEANER 315, an alkaline degreaser from Nihon Parkerizing Co., Ltd., by immersion at 60°C for 40 seconds in the 30 g/L bath. Degreasing was followed by a 30-second shower water rinse.

(2) Application and drying

I : The treatment bath, adjusted to a concentration of 16 mass%, was applied with a bar coater so as to give a dry coating thickness of approximately 1 μm . Drying was then carried out at a peak metal temperature (PMT) of 80°C.

II : The treatment bath, adjusted to a concentration of 16 mass%, was applied with a bar coater so as to give a dry coating thickness of approximately 1 μm . Drying was then carried out at a PMT of 150°C.

4. Evaluation methods

(1) Corrosion resistance

Corrosion resistance testing was run on the treated sheet samples prepared in the working and comparative examples using the following sample types: an unshaped (flat region) treated sheet sample, a treated sheet sample produced by the introduction using an NT cutter of a cross cut down to the basis metal (cross cut region), and a treated sheet sample produced by 7-mm Erichsen extrusion (shaped region). The corrosion resistance was evaluated as follows.

For the flat-region samples: The area of white rust development was determined after 72 hours of salt spray in accordance with JIS Z-2371, "Salt-spray testing methods". The area of white rust development was evaluated on the following scale.

area of white rust development

- ++ : less than 10%
- + : less than 30% but at least 10%
- Δ : less than 60% but at least 30%
- \times : at least 60%

For the cross cut samples: The state of white rust development was visually evaluated after 72 hours of salt spray in accordance with JIS Z-2371, "Salt-spray testing methods". The evaluation used the following scale.

state of white rust development

- 5
- ++ : almost no rusting
 - + : slight rusting
 - Δ : rusting occurred
 - × : substantial rusting occurred

For the shaped-region samples: The state of white rust development was visually evaluated after 72 hours of salt spray in accordance with JIS Z-2371, "Salt-spray testing methods". The evaluation used the following scale.

state of white rust development

- 10
- ++ : almost no rusting
 - + : slight rusting
 - Δ : rusting occurred
 - × : substantial rusting occurred
- 15

(2) Paint adherence

Using an NT cutter, a grid of 100 squares (1-mm square) was scribed on a painted test sheet (painting was carried out as described below) to a depth that reached the substrate. This grid was then subjected to tape peel testing using pressure-sensitive adhesive tape (primary adhesion). In another sequence, a grid was scribed in a painted test sheet; the sheet was immersed for 2 hours in boiling pure water; and the same tape peel testing was then executed (secondary adhesion). Evaluation was carried out by counting the number of paint grid squares remaining after tape peeling.

- 20
- ++ : 100
 - + : fewer than 100, but at least 80
 - Δ : fewer than 80, but at least 50
 - × : fewer than 50
- 25

30

Painting procedure: Using a bar coater, the surface-treated metal sheet was coated with DELICON #700 from Dainippon Toryo Kabushiki Kaisha so as to give a dry coating thickness of approximately 25 μm. Coating was followed by drying by baking for 20 minutes at 140°C.

35

(3) Fingerprint resistance

A finger was pressed onto the surface of the treated sheet followed by evaluation by visual inspection of the status of the residual fingerprint trace.

Evaluation scale:

- ++ : residual fingerprint trace entirely absent
- + : very faint residual fingerprint trace
- Δ : residual fingerprint trace present
- × : distinct residual fingerprint trace present

Table 3 reports the treatment bath composition and treatment method for the working and comparative examples that used a1 through a5 (polymers with general formula (I)) for the polymer (a), while Table 4 reports the same information for the working and comparative examples that used a6 through a12 (polymers with general formula (II)) for the polymer (a). Table 5 reports the results of the evaluations for the use of a1 through a5 as polymer (a), while Table 6 reports the results for the use of a6 through a12 as polymer (a).

As Tables 5 and 6 make clear, an excellent corrosion resistance, paint adherence, and fingerprint resistance were exhibited by the films afforded by the application of an inventive surface treatment agent (Examples 1 through 20) to the metal surface followed by drying.

In contrast, Comparative Example 1 (which lacked the organic polymer used as component (a) in Example 1) and Comparative Example 6 (which lacked the organic polymer used as component (a) in Example 11) both gave a poor corrosion resistance, paint adherence, and fingerprint resistance. A poor corrosion resistance was obtained in Comparative Example 2 (which lacked the metal compound used as component (b) in Example 2) and in Comparative Example 7 (which lacked the metal compound used as component (b) in Example 12). A moderately poor corrosion resistance and paint adherence were obtained in Comparative Example 3 (which lacked the component (a) of Example 6) and in Comparative Example 8 (which lacked the component (a) of Example 16). A poor corrosion resistance was obtained in Comparative Example 4 (which lacked both the components (a) and (b) used in Example 5) and Comparative Example 9 (which lacked both the components (a) and (b) used in Example 15). Finally, a poor corrosion resistance was obtained in Comparative Example 5 (which lacked the component (b) and optional component (c) used in Example 8) and in Comparative Example 10 (which lacked the component (b) and optional component (c) used in Example 18).

Table 3.

working and comp. examples	substrate	degreasing	treatment agent components (weight%)*					treatment method
			(a)	(b)	(c)	(d)**	other	
Ex. 1	A	(i)	a1 (88)	b3 (4) b7 (8)	---	---	---	I
Ex. 2	B	(i)	a2 (70)	b2 (16) b8 (14)	---	d1 (2)	---	II
Ex. 3	D	(ii)	a3 (80)	b2 (20)	---	d2 (3)	---	I
Ex. 4	A	(i)	a1 (40)	b3 (4) b7 (8)	c1 (48)	---	---	I
Ex. 5	B	(i)	a2 (20)	b2 (16) b8 (14)	c3 (50)	d1 (2)	---	II
Ex. 6	D	(ii)	a3 (35)	b2 (20)	c2 (45)	d2 (3)	---	I
Ex. 7	C	(i)	a4 (25)	b4 (15) b5 (15)	c3 (30)	d3 (5)	e1 (10) e2 (5)	I
Ex. 8	C	(i)	a5 (20)	b6 (4)	c4 (70)	d4 (2)	e2 (6)	I
Ex. 9	A	(i)	a3 (30)	b1 (4) b4 (4)	c1 (62)	d1 (4)	---	II
Ex. 10	B	(i)	a2 (10)	b3 (4) b7 (6)	c4 (80)	d2 (1)	---	II
Comp. Ex. 1	A	(i)	same as Example 1, but omitting component (a)					I
Comp. Ex. 2	B	(i)	same as Example 2, but omitting component (b)					II
Comp. Ex. 3	D	(ii)	same as Example 6, but omitting component (a)					I
Comp. Ex. 4	B	(i)	same as Example 5, but omitting components (a) and (b)					II
Comp. Ex. 5	C	(i)	same as Example 8, but omitting components (b) and (c)					I

* percentage calculated on the sum of the nonvolatile components of components (a) + (b) + (c) + (e) with the exception that (b) was calculated on the basis of the metal.

** concentration (g/L) in the treatment agent

Table 4.

working and comp. examples	substrate	degreasing	treatment agent components (weight%)*					treatment method
			(a)	(b)	(c)	(d)**	other	
Ex. 11	A	(i)	a6 (90)	b2 (5) b8 (5)	---	---	---	I
Ex. 12	B	(i)	a7 (80)	b2 (6) b7 (14)	---	d1 (2)	---	II
Ex. 13	D	(ii)	a8 (85)	b3 (15)	---	d2 (3)	---	I
Ex. 14	A	(i)	a6 (50)	b2 (5) b8 (5)	c1 (40)	---	---	I
Ex. 15	B	(i)	a7 (30)	b2 (6) b7 (14)	c3 (50)	d1 (2)	---	II
Ex. 16	D	(ii)	a8 (35)	b3 (15)	c2 (50)	d2 (3)	---	I
Ex. 17	C	(i)	a9 (50)	b5 (5) b8 (5)	c3 (25)	d3 (5)	e1 (10) e2 (5)	I
Ex. 18	C	(i)	a10 (20)	b6 (4)	c4 (70)	d4 (2)	e2 (6)	I
Ex. 19	A	(i)	a11 (30)	b1 (2) b4 (2)	c1 (66)	d1 (4)	---	II
Ex. 20	B	(i)	a12 (10)	b2 (2) b7 (1)	c4 (87)	d2 (1)	---	II
Comp. Ex. 6	A	(i)	same as Example 11, but omitting component (a)					I
Comp. Ex. 7	B	(i)	same as Example 12, but omitting component (b)					II
Comp. Ex. 8	D	(ii)	same as Example 16, but omitting component (a)					I
Comp. Ex. 9	B	(i)	same as Example 15, but omitting components (a) and (b)					II
Comp. Ex. 10	C	(i)	same as Example 18, but omitting components (b) and (c)					I

5

* percentage calculated on the sum of the nonvolatile components of components (a) + (b) + (c) + (e) with the exception that (b) was calculated on the basis of the metal.

** concentration (g/L) in the treatment agent

Table 5.

examples and comparative examples	corrosion resistance			paint adherence		fingerprint resistance
	flat region	cross cut region	shaped region	primary	secondary	
Example 1	+	+	+	++	+	+
Example 2	+	+	+	++	+	+
Example 3	++	+	+	++	++	+
Example 4	++	+	++	++	++	++
Example 5	++	++	++	++	++	++
Example 6	++	++	++	++	++	++
Example 7	++	+	+	++	++	++
Example 8	++	+	+	++	++	++
Example 9	++	++	++	++	++	++
Example 10	++	++	++	++	++	++
Comp. Ex. 1	Δ	×	×	Δ	×	×
Comp. Ex. 2	Δ	Δ	×	+	Δ	×
Comp. Ex. 3	Δ	Δ	Δ	Δ	Δ	+
Comp. Ex. 4	×	×	×	Δ	Δ	+
Comp. Ex. 5	Δ	×	×	+	+	Δ

Table 6.

examples and comparative examples	corrosion resistance			paint adherence		fingerprint resistance
	flat region	cross cut region	shaped region	primary	secondary	
Example 11	+	+	+	++	+	+
Example 12	+	+	+	++	+	+
Example 13	++	+	+	++	++	+
Example 14	++	+	++	++	++	++
Example 15	++	++	++	++	++	++
Example 16	++	++	++	++	++	++
Example 17	++	+	+	++	++	++
Example 18	++	+	+	++	++	++
Example 19	++	++	++	++	++	++
Example 20	++	++	++	++	++	++
Comp. Ex. 6	Δ	×	×	Δ	×	×
Comp. Ex. 7	Δ	Δ	×	+	Δ	×
Comp. Ex. 8	Δ	Δ	Δ	Δ	Δ	+
Comp. Ex. 9	×	×	×	Δ	Δ	+
Comp. Ex. 10	Δ	×	×	+	+	Δ

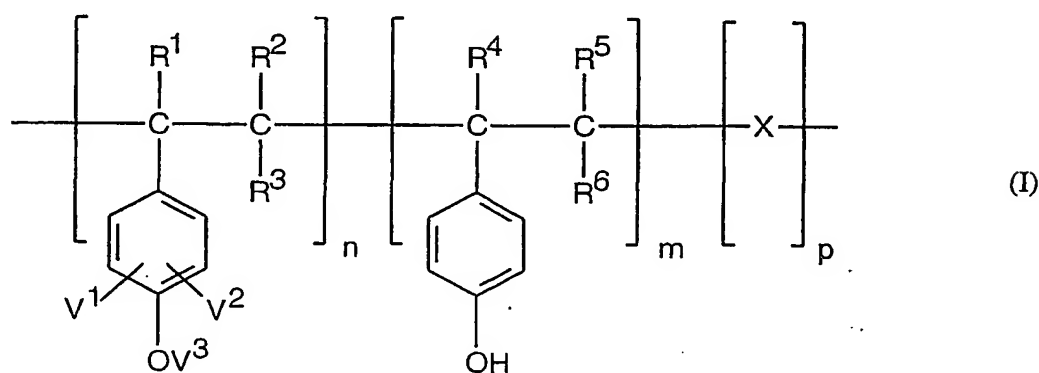
5

The surface treatment agent according to this invention is a nonchromium-type agent that is free of toxic chromium compounds. The coating formed from the inventive surface treatment agent has an excellent corrosion resistance, paint adherence, and fingerprint resistance. These features endow the inventive treatment agent and treatment method and the treated metals afforded thereby with a very high commercial and industrial utilization value.

10

What is claimed is:

1. An agent for treating metal surfaces comprising water and
 - (a) one or more polymers having general formula (I) or (II) as specified below; and
 - (b) one or more metal compounds containing at least one metal selected from the group consisting of vanadium, zirconium, titanium, molybdenum, tungsten, manganese, and cerium



wherein

R^1 through R^6 are each independently selected from H (hydrogen atom) and C_1 to C_5 alkyl;

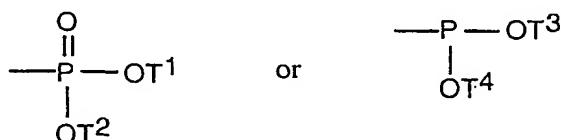
V^1 and V^2 are each independently selected from H (hydrogen atom), $-\text{CH}_2\text{OR}^7$, $-\text{Z}$, $-\text{OZ}$, $-\text{R}^8\text{Z}$, and $-\text{OR}^8\text{Z}$

wherein

R^7 represents C_1 to C_5 alkyl,

R^8 represents C_1 to C_5 alkylene, and

Z has a general formula as follows wherein T^1 to T^4 are each independently selected from H and C_1 to C_5 alkyl



V^3 is H or $-\text{Z}$ wherein this Z is defined as above;

at least 1 of groups V^1 through V^3 is a Z-containing functional group;

X is a group provided by the opening of an ethylenic double bond of an ethylenic double bond-functional compound that is different from both the compound that provides the structural unit encompassed by the subscript n and the compound that provides the structural unit encompassed by the subscript m ;

n is an integer from 2 through 50;

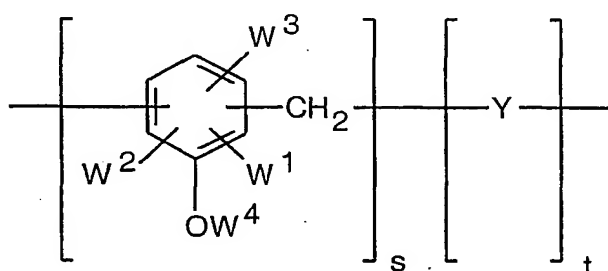
m is 0 or an integer from 1 through 50;

p is 0 or an integer from 1 through 20;

$0.1 \leq n/(n + m + p) \leq 1.0$;

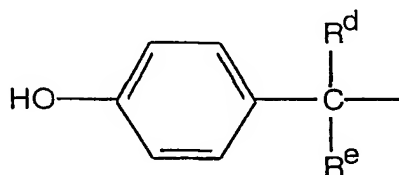
$0 \leq m/(n + m + p) \leq 0.9$; and

$0 \leq p/(n + m + p) \leq 0.6$;



wherein

W^1 through W^3 are each independently selected from H, $-\text{CH}_2\text{OR}^a$, $-\text{Z}$, $-\text{OZ}$, $-\text{R}^b\text{Z}$, $-\text{OR}^c\text{Z}$, and general formula (i)



wherein

R^a , R^d , and R^e are each independently selected from H and C_1 to C_5 alkyl,

R^b and R^c are each independently selected from C_1 to C_5 alkylene,

Z is defined as for Z in general formula (I), and

no more than 1 of W^1 through W^3 can be a group with general formula (i);

W^4 represents H or $-\text{Z}$ wherein this Z is defined as above;

at least 1 of groups W^1 through W^4 is a Z-containing functional group;

Y is a divalent group as afforded by removal of a hydrogen atom bonded to the aromatic ring carbon of an aromatic compound capable of undergoing addition

condensation with formaldehyde, said divalent group being different from the aromatic ring moiety in the structure encompassed by the subscript s, or Y is a divalent group as afforded by the removal of one hydrogen atom from each of the 2 amino groups in melamine, guanamine, or urea;

5 s is an integer from 2 through 50; and

t is 0 or an integer from 1 to 20.

2. The agent of claim 1 additionally comprising at least one organic polymer (c) selected from the group consisting of anionic organic polymers and nonionic organic polymers.

10 3. The agent of claim 1 or 2 wherein at least one of the metal compounds is a vanadium compound containing vanadium in a trivalent or tetravalent oxidation state.

4. The agent of claim 1, 2 or 3 additionally comprising one or more fluorine compounds.

15 5. The agent of claim 1, 2, 3 or 4 having a mass ratio of metal compound (b) (as metal): polymer (a) which is from 0.005 to 2.0.

6. The agent of claim 1, 2, 3, 4 or 5 additionally comprising one or more water-dispersible sols selected from the group consisting of silica sols and metal sols.

7. The agent of claim 1, 2, 3, 4, 5 or 6 additionally comprising one or more waxes.

20 8. A method for treating a metal surface comprising of the steps of:
forming a coating of the agent according to claim 1, 2, 3, 4, 5, 6 or 7 on a metal surface; and
drying said coating by heating so that said metal surface reaches a temperature of 50°C to 250°C.

25 9. A metal bearing a coating formed using the method of claim 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/17408

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C23C 22/00

US CL : 148/251

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/251, 247, 273; 106/14.21, 14.44

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,125,989 A (HALLMAN) 30 June 1992 (30.06.1992), abstract, col. 3, lines 4-5 and 20-35 and 65-68, col. 4, lines 40-42, col. 5, line 36.	1, 4-5 and 8-9
X	US 4,457,790 A (LINDERT et al) 3 July 1984 (03.07.1984), abstract, col. 2, lines 15-45.	1, 4-5 and 8-9
Y	US 5,449,415 A (DOLAN) 12 September 1995 (12.09.1995), abstract, col. 2, line 11 to col. 3, line 20.	1, 3-5 and 8-9
Y	US 4,433,015 A (LINDERT) 21 February 1984 (21.02.1984), abstract, col 1, lines 7-13, col. 1, line 65 to col. 2, line 30.	1, 3-5 and 8-9
A	US 5,246,507 A (KODAMA et al) 21 September 1993 (21.09.1993), abstract, col. 2, lines 43-44. Table 1K and 1L.	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:		"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

10 July 2001 (10.07.2001)

Date of mailing of the international search report

02 AUG 2001

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks

Box PCT

Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer

Andrew L Oltmans

Telephone No. 703-308-0661

DEBORAH THOMAS
PARALEGAL SPECIALIST

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/17408

Continuation of B. FIELDS SEARCHED Item 3:

EAST, STIC

polymer structure search

additional search terms: metal, treatment, surface, resin, polymer, vanadium, zirconium, molybdenum, tungsten, manganese, cerium

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